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STREAM POLLUTION HAZARDS OF WOOD PULP MILL EFFLUENTS

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Introduction

In the United States the production of wood pulp which started with a few ground-pulp mills in the northern forest areas has grown into one of the Nation's major chemical industries. An increasing demand for paper and wood-pulp products resulted in the development of several chemical processes which gave great impetus to wood pulp production. Although these chemical operations, particularly the sulfite process, increase the efficiency and the output of the pulp industry, they have brought with them wastes which present difficult disposal problems. Following the precedent set by other industries, these wastes in many cases have been flumed into streams and serious pollution conditions have resulted.

With the development by industrial chemistry of commercial rayon and cellophane plants a still greater demand for wood pulp has been created in the past few years, so that the pulp industry is now expanding into new locations. These new pulp mills are economically very desirable, but they have magnified the stream pollution problem because of the increasingly larger volumes of chemical effluents for which the pulp industry must find an outlet.

As there are several types of pollution hazards presented by the pulp mill effluents and as some of the effects of these wastes are cumulative rather than immediate, the detrimental action of these pulp effluents on fish and other aquatic life cannot be measured by any single standard. Consequently in this memorandum the details of the hazards to fish life produced by the several kinds of wastes from pulp mills are reviewed individually.

In presenting the major pollution hazards which may be expected when wood pulp effluents are introduced into streams and other waters, average conditions are discussed. Industrial processes are not fixed entities, however, and the details of individual plant procedures not

only vary but are changed frequently in the interest of efficiency and economy. Consequently specific applications of these statements of hazards can only be made when supporting data on both local stream conditions and the operations of the concern in question have been considered, as wood pulp effluents are not uniform in composition, concentration, or in degree of detrimental action.

METHODS OF WOOD PULP PRODUCTION AND THEIR EFFLUENTS

Four processes and various combinations of these are used currently in the production of commercial wood pulp, and the effluents differ accordingly.

Ground Wood Pulp

Ground wood pulp is made by pressing logs against revolving grindstones, a stream of waterwashing away the pulp and depositing it on screens. The waste water from this process carries some pulp and wood dust which passes the screens and varying amounts of the soluble extractives from the wood depending upon the quantity and temperature of the water used, the kind of wood being ground, and the previous treatment of the logs, i. e. whether they were steamed, soaked or dried before grinding. Even though this method usually includes no extensive addition of chemicals, the aqueous solution carrying extractives from such finely divided woods, especially of pine, is often somewhat toxic to the aquatic organisms coming in contact with it.

Soda Pulp

Soda pulp is produced by digesting wood chips in a strong solution of caustic soda, the process being expedited by the use of heat and pressure. The pulp is recovered on screens from a strongly alkaline brownish liquor of high specific gravity containing a large number of organic compounds derived from the disintegrated wood. The soda liquor which always contains some unrecovered pulp is therefore a mixture of very variable composition depending upon the kind of wood as well as upon the duration of the digestion period, the strength of the alkali and other factors. As a large percentage of the soda liquor is recovered at the plant (at least 95 percent, Witham, 1942) the effluents from soda pulp mills are chiefly alkaline wash waters carrying varying amounts of diluted soda liquor containing extractives from the wood together with such pulp as is lost through the screens.

Sulfite Pulps

Sulfite pulps are obtained by the action of lime and magnesia bisulfites on wood chips in the presence of excess sulfur dioxide in solution, aided by heat and pressure. After recovering the pulp on screens a strongly acid fluid remains which includes in its large and variable list of components the disintegration products of the wood many of which are sulfonated, several types of sulfur compounds, some pulp, and a large amount of extractives. Although some of the sulfite liquor is reclaimed or otherwise used at present, the effluents from sulfite mills include the sulfite liquor, various wash waters used in removing the sulfite liquor from the pulp, a large amount of wood extractives in solution and always some pulp.

Sulfate Pulps

Sulfate pulps used in the manufacture of the Kraft papers are the products of a process which combines some of the active agents from both the soda and sulfite processes, as incompletely reduced sodium sulfate (salt cake), i.e., a mixture of sodium sulfate, sodium sulfide, sodium carbonate and sodium hydroxide together with variable quantities of the complex sulfates and sulfites, is used as the digestant for the wood chips. After removal of the sulfate pulp a waste fluid called "black liquor" remains which is alkaline in reaction and carries a variety of compounds some of them sulfonated, resulting from the disintegration of the wood in the digester. Since Kraft pulps are usually not cooked out as completely as sulfite pulps, the organic content of the black liquor is generally not as high as that of the sulfite liquor.

In contrast to the sulfite process, the waste from the sulfate process does not contain nearly as large a percentage of organic material and chemicals, for the recovery of heat energy and chemicals from the spent liquor by evaporation and burning is one of the outstanding features of the sulfate method. In fact Witham (1942) refers to various types of recovery systems which save 95 percent of the chemicals or in some cases even more. Sutermeister (1941) considers a loss of 40 pounds of salt cake per ton of fiber produced an indication of superior operating conditions. Although the percentage of chemicals and extractives lost is relatively small, the load entering the stream via the waste from the plant, when hundreds of tons of pulp are produced daily, can be quite large indeed.

EFFECTS OF PULP MILL EFFLUENTS ON AQUATIC LIFE

The effluents from all of the processes enumerated are damaging to aquatic life because of the pulp fibers which are lost, the oxygen demand of the unstable compounds liberated from the wood or produced during the operations, and the specific toxic action of various substances.

Blanketing Effect of Wood Pulp

The introduction of wood pulp into streams and other waters, and all pulp mills lose some pulp, is dangerous to aquatic life largely because cellulose fibers do not disintegrate rapidly in the water and therefore accumulate, covering submerged objects and blanketing the stream floor. These layers of wood pulp decrease the productivity of the stream by smothering out large numbers of food organisms, by covering spawning beds, and by harboring undesirable fungi and bacteria. Vallin (1939) emphasized that fibers collect slime and detritus and destroy the bottom life on which fish subsist. As pulp fibers readily mat down with silt and sewage, wood pulp also greatly increases the pollution hazards from these sources.

Experimental work has shown that healthy adult fish of several species may survive in suspensions of wood pulp for 20 days or more without apparent damage if the gill action of the fish is good. These tests have been offered repeatedly as showing that wood pulp is not

injurious to fish life. It has also been established, however, that young fish often become hopelessly entangled in mats of wood pulp, and that the gills of both young and adult fish are speedily clogged with wood pulp fiber if the fish is incapacitated even for a short time or weakened.

It has also been pointed out that wood pulp is readily carried away by current action in rapid streams. This is true, but U. S. Fish and Wildlife Service field parties working in Maine and other parts of the country found that wood pulp, although very largely washed away from the immediate vicinity of flumes entering streams with strong currents, was deposited in slack waters sometimes 15 to 20 miles downstream from the point of entrance. In these quieter portions of the rivers not only was the stream floor covered with pulp fiber but near the coast where tidal action and brackish water added factors which complicated the stream flow layers of dense pulp suspensions filled the pools and lower portion of the stream bed for a vertical distance of 3 to 6 feet above the river floor.

Both field and experimental data show that in general, the detrimental effects of wood pulp on stream conditions as a whole and therefore on the productivity of the stream have been under-estimated chiefly because the fibers do not kill adult fish immediately. Fortunately wood pulp is the saleable product of the pulp mills and the pulp industry has realized the enormous loss which it formerly suffered through the unreclaimed pulp in the "whitewater." Less pulp is lost each year but it should be remembered that owing to the cumulative build-up of pulp deposits very small amounts of pulp if supplied continuously can ultimately produce serious damage to fish life in almost any stream.

Reduction of Dissolved Oxygen in Stream Water

The liquid portions of pulp mill effluents carry various unstable and unoxidized compounds (largely organic substances leached or chemically dissolved from the wood during the production of the pulp) having high oxygen demands. These substances readily remove the dissolved oxygen from the waters of streams receiving pulp wastes so that aquatic life in streams thus polluted may face conditions ranging from unfavorable to asphyxial as regards the dissolved oxygen. This importance of the oyxgen demand is well known to the paper industry (Technical Association of the Pulp and Paper Industry 1943) and to aquatic biologists.

Several factors determine the rapidity of the reaction of those compounds having high oxygen demand with the dissolved oxygen in the stream water but analyses made in Maine and Wisconsin show that sulfite liquor as taken from the digesters of wood-pulp plants operating in these states has an average one-day oxygen demand of approximately 1,500 parts per million, although many samples run much higher (up to 8,000 p.p.m.) and others much lower. Using this gross average value of 1,500 p.p.m. for a one-day oxygen demand, it may be seen that sulfite liquor could produce very disastrous effects on fish life through the reduction of the dissolved oxygen if poured into stream waters, since

the average dissolved oxygen content of streams supporting fish life in the United States lies between 4 and 9 p.p.m. and a reduction of the dissolved oxygen to 3 p.p.m. produced conditions not only unfavorable but approaching the critical for many fishes. Actual tests and field observations have shown that under average conditions a dilution of sulfite liquor to 1:200 in the stream is usually sufficient to meet the oxygen demand of this waste without lowering the dissolved oxygen of the stream to a critical point, provided adequate mixing is assured.

Comparing the four types of pulp effluents, sulfite liquor usually has the highest oxygen demand. Sulfate black liquor and the alkaline soda liquor generally have less oxygen demand than sulfite liquor and ground wood pulp effluent although sometimes having an oxygen demand equal to 10 percent of that of sulfite liquor may run as low as 2 percent or less in relative oxygen demand. The proportionately low oxygen demand of ground wood pulp water is not surprising when it is remembered that no chemicals are used in this process. These comparative values although giving some idea of the relative magnitude of the oxygen demands of the four major pulp effluents must be used with caution since so many variables are involved.

Toxic Effects of Dissolved Substances

The specific toxicities of the four major types of pulp effluents are considered separately because of differences in reaction and chemical composition.

In discussing the lethal concentrations of these effluents the dilutions are always expressed in terms of the unmixed liquid waste as drawn from the digester. As has been pointed out repeatedly, however, even digester liquors are not constant in composition and as several at least of the known toxic components of these wastes are volatile, through aeration and handling of samples drawn directly from the same digester, it is possible to obtain wide variations in the apparent toxicity of liquors from one run of pulp. Consequently, the average values given can only be used to estimate the expected magnitude of toxicity. It must be remembered, also, that the oxygen demand of the waste and its specific toxicity are independent variables. Oxygen demand cannot be used as an index of even relative toxicity since some of the most toxic components of these wastes do not produce any oxygen demand.

Ground wood pulp waste.--The dissolved substances in ground wood pulp waste waters vary greatly with the kind of wood, but since only water is used in the process and the logs are peeled before grinding, these effluents are usually low in specifically toxic substances, and if the pulp fiber hazards are eliminated by proper screening and the oxygen demands of these waste waters are met by adequate dilution ground wood pulp waters present little in the way of pollution problems from toxic constituents. These statements, however, do not apply to the steepings from bark nor the leachings from logs which are pre-treated with steam or boiling water. Some confusion has arisen concerning the toxicity of ground wood pulp effluents because ground wood pulp mills maintain subsidiary divisions in their plants which use bark or which specifically treat some kinds of logs. Wastes from these particular

processes, which are not of course pulp processes, are often very toxic to fish and other aquatic life either alone or when mixed with run-off waters from the pulp grinding.

Sulfite liquor.--Sulfite liquor is strongly acid and if large quantities of the digester liquor be poured into the stream, fish in the immediate vicinity of the outlet may be killed by the hydrogen ion effect of this effluent before it is diluted and buffered by the stream water. It is difficult to state where the dominant effect of the acids in the sulfite liquor leave off and the more specific effects of other substances in this waste begin, but in concentrations more acid than pH 6 acidity is at least a contributing factor to the lethal action of sulfite liquor. If this waste is neutralized, however, it still retains its toxic properties so that the contained acids are only one group of toxic ingredients.

Experiments carried out by various observers and at U. S. Fish and Wildlife Service laboratories indicate that the maximum concentration of sulfite liquor, i. e., full strength as drawn from the digester, in which if the dissolved oxygen is properly maintained warm water fish will survive for 10 to 20 days, is between 1:200 and 1:500. Trout and other cold-water fish under the same conditions succumb in a few days, however, to a concentration of 1:1,000. These figures give the general range of dilution required if immediate injury to fish fauna is to be avoided.

It has been noted repeatedly, however, that both the fish fauna and the food organisms gradually decline in streams carrying much less sulfite liquor than indicated by the above dilutions. These observations suggest that there are cumulative effects from prolonged exposures to even very small quantities of sulfite liquors. Recent experiments have confirmed this conclusion, as serious chronic effects on various internal organs of fish have been found following long exposures to low concentrations of sulfite liquor. Although no maximal non-harmful concentration for sulfite liquor can be stated definitely at this time dilutions as high as 1:100,000 are known to have produced definite damage to warm water fish.

Sulfate waste.--Black liquor or sulfate waste is usually quite alkaline and if poured into streams in quantities large enough to raise the alkalinity of the water to pH 8.7 or above, has a definite hydroxyl effect. This waste is lethal only in strong concentrations (Liebmann, 1941). The alkaline substances in the sulfate wastes, however, act synergically, particularly in damaging the gills and other structures secreting or covered with mucous, with other toxic agents in this liquor even at hydroxyl concencentrations which are ordinarily tolerated by fish. As a result, injuries produced by exposure to very dilute black liquor may lead later to the death of the fish from other causes which can strike through the weakened or damaged part.

Comparatively, the sulfate liquor is more toxic in its immediate effects than the sulfite liquor (Vallin, 1935). In the Fish and Wildlife Service laboratories, concentrations of the sulfate liquor of 1:500 to 1:1,000 are lethal for some warm water fish in less than 1[illegible] days even when proper provision is made to maintain a suitable amount of dissolved

oxygen. Both field and laboratory work show that continued exposure to small quantities of sulfate liquor produces cumulative effects in fish and various food organisms. Again it is impossible at this time to state definitely the maximal non-harmful concentration of this waste but internal systemic derangements have been observed in fish exposed to 1:100,000 dilution of sulfate liquor and it seems probable that even smaller quantities of sulfate liquor may have serious effects on fish life through cumulative action.

Soda pulp waste.---Soda pulp waste as far as tested seems about midway between sulfate and sulfite wastes in immediate toxicity, if the excess alkali be neutralized. Samples of this alkaline waste studied have carried less volatile toxic material than either of the other two chemical pulp wastes. At present little can be said concerning the cumulative action of soda pulp waste, but streams which have received even small quantities of this effluent have shown the same decrease in fauna and productivity characteristic of streams polluted with the other chemical pulp wastes. Fortunately little soda liquor is lost.

Accessory substances.--Two other pollution hazards must be noted because they sometimes complicate the interpretation of the dangers of pulp mill effluents. Many pulp plants bleach their pulps, and free chlorine together with various chlorine bleaching powders may be found in the effluents from these mills. Free chlorine is highly toxic to fish, 1 p.p.m. or less being lethal for many warm water fish, and much lower concentrations are detrimental to various food organisms. In addition chlorine may form chloramine in the presence of certain ammoniacal compounds, which is even more toxic, as 0.06 p.p.m. of chloramine can kill trout and 0.4 p.p.m. warm water fish.

Some mills manufacture both pulp and paper, and the pulp is treated either before or after calendering with various fillers, sizings, coatings, and even dyes. Many of these substances are highly toxic to fish, and as the waste waters from such plants may carry any or all of these pulp-processing materials the effluents from pulp mills which also manufacture paper often present pollution problems quite different from those described for pulp wastes alone.

Odors

It is well known that wastes from paper mills have characteristic unpleasant odors. In fact, Jarnefelt (1936) working with the effects of waste waters from cellulose plants on plankton and salmon found that there was a taste in the flesh of the fish exposed to the waste, which he attributes to turpentine material from the waste waters. Furthermore, when the products from paper mills gather, stagnate, and disintegrate along the bottom below the paper mill, the fishes caught in these areas often have a taste similar to the odor of the paper mill.

SUMMARY

The hazards to fish and other aquatic life from pulp mill effluents may be briefly summarized as follows:

(1) Loose fiber pollution, producing mats on the bottom of the stream and on submerged objects, with resultant destruction of fish, food and spawning grounds, and direct damage to the fish themselves.

(2) Immediate toxic effects produced by the wood extractives, disintegrating substances and chemical waste products contained in the spent liquor from the digesters and in the wash waters.

(3) Reduction of dissolved oxygen in the stream water because of the oxygen demands of various organic substances in these pulp wastes.

(4) Cumulative toxic effects, even in very high dilutions of these wastes, due to the specific toxic action of several organic substances produced or liberated by the chemical digestion of the wood.

(5) Specific toxic action of various accessory substances used in the manufacture and processing of paper and other pulp products.

(6) An unpleasant taste often found in the flesh of fish caught in a stagnant area below the paper mill.

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